THE MELTING AND PYROLYSIS OF TEFLON AND THE MELTING OF SILVER CHLORIDE AND IODINE UNDER HIGH PRESSURE*

BY MASAOKI TAMAYAMA, TERRELL N. ANDERSEN, AND HENRY EYRING

INSTITUTE FOR THE STUDY OF RATE PROCESSES, UNIVERSITY OF UTAH, SALT LAKE CITY

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The melting temperatures have been determined for a wide range of substances as a function of pressure. In the present work, Teflon (polytetrafluoroethylene) was investigated up to 30 kb and the decomposition temperatures, and the melting temperatures of silver chloride and iodine were determined up to 30 kb and 20 kb, respectively.

General Technique.—The pressure was generated with a piston-cylinder type press, the details of which can be found elsewhere.¹⁻³ A typical high-pressure furnace is shown in Figure 1. The temperature of the sample was varied by means of an electrical resistance graphite heater placed in the high-pressure furnace. Electricity was applied to the heater at a constant rate. Two Alumel-Chromel thermocouples were set in the furnace, one for measuring the temperature of the sample and the other to be used in making a differential thermal analysis (DTA). The slight change of electromotive force of the thermocouples due to pressure⁴ was not corrected for in the present work.

The high-pressure furnace used in the present work consisted of materials such as talc, pyrophyllite, graphite, and Teflon, which served as solid pressure transmitting media. The calculated pressure at the bottom of the moving piston is not transmitted unchanged through such highly viscous pressure transmitters as are used in our high-pressure furnace. There are at least three major factors to be considered. The first factor is the pressure loss due to an interfacial friction between the cylinder wall and the piston surface including the influence of the packing material leaking into the clearance between the piston and the cylinder. The second factor is the pressure loss due to an interfacial friction between the cylinder and the medium used for the outside of the high-pressure furnace. The third factor is the pressure loss due to the shearing or flow properties of the media used. These pressure losses, however, have been carefully studied.¹

The total pressure losses were determined as 3.7, 5.5, and 6.6 kb at the gauge pressures 5.0, 10.0, and more than 15.0 kb, respectively, in the high-pressure furnace shown in Figure 1. These values were applied to determine the phase diagram of bismuth and were found to be valid. Therefore, the above values of pressure losses were applied in the following experiments to calibrate the gauge pressures, which were read from a 16-in. diameter Heise gauge set in the primary hydraulic oil line.

Samples.—(a) Polytetrafluoroethylene: DuPont's Teflon rod. (b) Silver chloride: 99.992 per cent minimum purity, reagent. (c) Iodine: 99.85 per cent minimum purity, resublimed crystals, analytical reagent.

TEFLON (POLYTETRAFLUOROETHYLENE)

The phase diagram of Teflon has been determined by Weir⁵ and Beecroft and Swenson.⁶ Three solid phases were found.

Experimental.—As a typical property of high polymers, Teflon did not show clear solid-solid transitions or melting temperatures. The thermal decomposition

temperatures were very clearly observed. Figure 2 shows the sample temperatures (*solid line*) and the DTA (*broken line*) at 13.7 kb.

The sample temperature rose smoothly up to 485°C, then began to show an endothermic transition as shown by a decrease in curvature. The curvature again changed at 645°C and the sample temperature increased smoothly up to 760°C. The temperature range from 485 to 645°C is interpreted as showing the melting phenomenon of Teflon. The sample temperature versus time curve rose abruptly at 760°C.

This indicated an unusual temperature increase in the Teflon sample. Examinations after this abrupt temperature increase showed that no Teflon remained; instead, a soft lump of black powder and acidic fumes were left in the high-pressure furnace. Therefore, the beginning temperature of the sharp increase appears to correspond to the thermal decomposition of Teflon at that pressure.

The changes in the Teflon sample, with increasing temperature, can be better understood by examining the corresponding DTA curve simultaneously with the temperature curve. Pyrophyllite, used as a reference material, has very little interlayer water in the structure, and dehydration of hydroxyl water, which shows an endothermic reaction on the DTA curve, occurs above 700°C at atmospheric pressure.^{7, 8} The DTA curve in Figure 2 shows a very small endothermic transition which corresponds to the sample temperature from 245 to 310°C. This endothermic transition which was observed in three out of five runs at different pressures is presumably to be assigned to the Teflon I-III transition (Fig. 3).

The DTA curve began to show another endothermic transition at the sample temperature of 460°C. In all runs of Teflon the temperature of the DTA curve began to lower around the point on the heating curve corresponding to the beginning of decreased curvature, and the deepest point of the DTA curve corresponded to a point midway between the two points of rapidly changing curvature. This indicates that the melting began at the first point of rapidly changing curvature and terminated between the mid-point and end of the final point of rapidly changing curvature. The DTA curve shows that the temperature of the molten Teflon first increases fairly rapidly and then abruptly at 760°C. This same abrupt rise is also observed on the temperature-time curve of the sample.

Results.—In Figure 3 several pressure vs. temperature curves are shown. The phase diagram of Teflon by Beecroft and Swenson⁶ was drawn at the bottom, left corner, and is enclosed by a broken line. The

FIG. 1.—High-pressure furnace.

FIG. 2.—Experimental curves of Teflon at 13.7 kb.

FIG. 3.—Phase diagram of polytetrafluoroethylene (Teflon). ○, Present work; □, McGer and Duus; △, Schwenker and Zuccarello; ▽, Doyle.

the completion of melting. The points on this line correspond to the final point of rapid change of curvature on the temperature-time curve of the sample for a particular pressure. As the representative melting temperature of Teflon, a line was drawn through the middle of the melting zone.

The top curve in Figure 3 shows the thermal decomposition temperature of Teflon as a function of pressure. The points, lying on this line, correspond to the temperatures where the recording pen rose abruptly on the temperature-time curve for a particular pressure.

Discussion.—(1) *The Teflon I-III boundary:* Only weak signals appeared on the DTA curves. The left end of the boundary curve overlaps previous work.⁶ This gives support to our method of pressure calibration.¹ With increasing pressure the temperature range of the Teflon I-III transition widened and became less clear. For the high-pressure range as well as the very low pressure range experimental techniques^{9, 10} should be improved. This would include work on an improved furnace design, on the best heating rate, on the best sample size, and on increasing the sensitivity of the recorder.

(2) *Melting:* The melting temperature of Teflon is 327°C at atmospheric pressure within experimental error.¹¹ The DTA experiment by Paciorek *et al.* shows 325 and 344°C for the beginning and ending temperatures of melting, respectively.¹² The corresponding temperatures determined by Schwenker and Zuccarello are 280 and 343°C. They used a bulk sample of Teflon in a nitrogen atmosphere.¹³ McGer and Duus have studied the pressure dependence of the melting of Teflon in the lower region of high pressure.¹⁴ The values found for melting are 324, 335, 356, and 419°C at 1, 69, 207, and 615 atm, respectively. They took the mid-points of the abrupt change of specific volume on the specific volume-temperature curves of the sample as the true average melting temperatures of

boundary of the Teflon I-III transition was extended, and the melting temperature zone and thermal decomposition temperature of Teflon were determined in the present work. The vertical lines on the boundary curves between Teflon I-III show the transition temperature range taken from the temperature-time curves like the one shown as the unbroken line in Figure 2. Beyond 15 kb it was quite difficult to determine the Teflon I-III transition by the DTA method used here.

Three lines were drawn to indicate the melting behavior of Teflon. The lowest line shows the beginning of melting. These temperatures correspond to the beginning of the endothermic transition observed on the temperature-time curve for the sample and on the DTA curves (see Fig. 2). The points on the melting curves do not lie exactly on a line, but they do show the tendency of increasing temperature of melting with increasing pressure. The third line shows

Teflon. Their observation of melting can be smoothly connected to our "representative melting curve" (see Fig. 3). Also, our curve for the "beginning of melting" (see Fig. 3) extrapolates well to the 280°C at atmospheric pressure found by Schwenker *et al.*¹³ Connecting our curve for the ending of melting to 343°C found by Schwenker *et al.* is inappropriate because of the large differences in heating rate in the two types of experiments near the end of melting.

The sharp effect of pressure on the melting temperature of Teflon up to about 2 kb is quite unique. The curve labeled "representative melting curve" in Figure 3 is the safe temperature-pressure limit to which Teflon can be used as a structural material for high-pressure furnaces. Teflon was used as a sample container up to the curve indicated by "melting ends" to determine the melting temperatures of iodine under high pressure. "Melting" of Teflon is actually the loss of crystallinity, but not the formation of a true liquid. The outstanding properties of Teflon are very high viscosity¹⁵ (10^{11} poise at 350°C and at atmospheric pressure), large molecular weight¹⁶ (6×10^6 to 10×10^6), and its extremely poor reactivity with any chemical. These properties make the plastic a good sample container for high-pressure research even when Teflon is in the noncrystalline state. If a sample is enclosed in a container made of Teflon and the reference material is outside this container, the small thermal conductivity of Teflon¹⁷ (6×10^{-4} cal·cm⁻²·sec⁻¹·°C·cm⁻¹ at atmospheric pressure) makes it possible to obtain sharp DTA peaks on heating and cooling.

(3) *Pyrolysis*: The thermal decomposition or degradation of polytetrafluoroethylene (Teflon) has been studied by a number of investigators.^{13, 18-24} Teflon is not combustible in air and when heated on an evaporating plate it leaves very little residue. The degradation of Teflon begins at 423.5°C, but the rate is extremely slow.¹⁸ The temperature range of pyrolysis has been extended to 1,200°C.¹⁹ The degree of degradation of Teflon depends on the temperature and the procedure adopted. Doyle devised a comprehensive index of thermal stability of high polymers under definite procedural conditions.²⁰ According to this index, "the integral procedural decomposition temperature," is 555°C for Teflon in a nitrogen atmosphere. Schwenker and Zuccarello reported that a bulk sample of Teflon began to depolymerize at 525°C.¹³ This endothermic peak was followed by a very large exothermic peak at 602°C suggesting the formation of new products in the nitrogen atmosphere. In the present work an endothermic peak, such as that shown by Schwenker and Zuccarello's DTA, was only observed in the run carried out at the lowest pressure of 1.8 kb. The endothermic reaction began at 670°C and ended at 685°C. At the higher pressures this type of endothermic reaction was not observed.

The most noticeable effect of high pressure on the decomposition of Teflon is the appearance of a carbon residue which is absent when the Teflon is decomposed in vacuum. It has been reported that the pyrolysis products of Teflon will vary with temperature¹⁹ and pressure.²¹ However, the products reported have always been fluorocarbons such as C₂F₄, C₃F₆, C₄F₈, and higher molecular weight compounds. CF₄ was obtained in decompositions carried out at high temperatures.¹⁹ However, the reactions proposed by previous workers do not include the formation of carbon as a product.

The unzipping mechanism, presented by Friedman,²² explains Madorsky's

observations in which pyrolysis of Teflon was carried out in vacuum over a temperature range of 423.5–517°C.¹⁸ Goldfarb *et al.* suggested that a radical formed as the result of a carbon bond breakage could extract a fluorine from a neighboring molecule. The fluorine-deficient radical then decomposed into a radical with a free carbon bond and a molecule having an end double bond.²³ They also suggested the volatilization of large molecules.

Lewis and Naylor showed that the pyrolysis products of Teflon depend on the applied pressure in a range of 5–760 mm Hg.²¹ The pyrolysis products of Teflon also depend on the temperature of decomposition, even when the decomposition occurs in vacuum. Straus and Madorsky observed decreasing fractions of C₂F₄ and increasing fractions of CF₄, C₃F₆, and larger fragments with increasing temperature.¹⁹ HF was observed in the products at 1,200°C.

An interesting fact concerning the pyrolysis of tetrafluoroethylene, CF₂ = CF₂, the monomer of Teflon, has been reported. In the pyrolyses of perfluoro compounds very little carbon collects in a trap during any hot-tube reactions at temperatures ranging from 435 to 750°C.²⁵ On the other hand an explosive reaction,

has been observed at a high temperature and high pressure, but the paper gives no detailed experimental data.¹⁵

Returning to our high-pressure experiments, we observed that carbon occupied all of the space formerly occupied by the Teflon sample whether the decomposition occurred at 1.8 kb where DTA revealed two successive endothermal processes, or at higher pressures where only one endothermal process is observed. The endothermic reactions are followed by an exothermal one which presumably involves the pyrophyllite. From these observations several conclusions can be drawn concerning the pyrolysis of Teflon under very high pressure.

The first endothermal reaction observed at 1.8 kb is probably a chain-breaking reaction.^{13, 22, 23} Subsequently the radicals decompose, yielding carbon. The DTA curves fail to separate the two endothermal decomposition reactions at 5 kb. Other fluorocarbons, HF, CO, CO₂, and the silicon fluorides are to be expected from reaction with pyrophyllite. Reaction (1) is considered as an intermediate step for the formation of carbon, but Lewis and Naylor's results²¹ showed that very little CF₂ = CF₂ is to be expected under very high pressures.

The present high-pressure furnace and apparatus are not adequate to investigate gaseous products. This limitation prevents a more detailed discussion of the mechanism of pyrolysis of Teflon.

FIG. 4.—Phase diagram of silver chloride.

SILVER CHLORIDE

Silver chloride is an important compound in high-pressure research due to its quasi-hydrostatic

nature under high pressure, but its melting parameters have been previously discussed only at atmospheric pressure.²⁶ A thermocouple for DTA was unnecessary because the melting temperature is clearly observed as a break in the regular heating curve. The melting zone of silver chloride was wide but the beginning temperature of melting at each pressure, i.e., the beginning point of reduced curvature, was taken as the melting temperature. The resulting phase diagram is shown in Figure 4.

IODINE

Some properties of iodine have been studied under high pressure.²⁷⁻³¹ When the present paper was submitted to the Spring Meeting of the Salt Lake Section of the American Chemical Society (convened at the University of Utah in May of 1966), a paper on the melting of iodine at high pressure had just been published by Klement, Cohen, and Kennedy.³¹ The most interesting point is the large difference in melting temperatures obtained by them and by us.

Experimental and Result.—Some difficulties were found in measuring the melting temperatures of iodine in the present work. These difficulties arose from leakage of the sample container, reaction with the thermocouple, and the manner of preparation of the sample. The sample preparation problem was solved by using a special die which consisted of Teflon alone.¹ One gram of iodine was used for each run.

The prevention of leakage of iodine at the melting point was important because leakage resulted in a much lower observed melting temperature. When pyrophyllite was used as a sample container, penetration of iodine into it was serious at the melting point. The melting phenomenon was then observed as a two-step process and the solidification temperature was difficult to determine. On the other hand, when Teflon was used as the container, the melting was observed as a one-step process and produced a large signal on the DTA as shown in Figure 5. The height of the DTA peak usually ranged from 75 to 170°C and large supercooling effects were observed.

A study was made of the thermocouple readings. A thermocouple was set directly in the iodine during a run. In another run a thermocouple tip was set in a tantalum plug whose tip was surrounded by iodine. No differences were found in the temperatures in the two cases, though the signal on melting in the latter case was small. Then the "spoiled" thermocouple set in the iodine was calibrated with a normal one. There were no differences in the temperatures indicated by the two thermocouples, but the spoiled thermocouple wires, especially Alumel, became weak and brittle. As a result of the above observations an Alumel-chromel thermocouple was usually placed in iodine.

The temperatures at the beginning of melting are taken as the melting temperatures and are plotted in Figure 6. Each melting temperature was obtained by using a new sample to reduce the effects of the spoiled thermocouple, even though such effects were assumed to be nil.

Discussion.—The large differences between the data of Klement *et al.* and the present data must be discussed. The temperature differences are 40, 80, and 130°C at 5, 10, and 15 and 20 kb, respectively (our melting temperatures are higher at a given pressure). Another possibility is that the temperatures are all right

FIG. 5.—Experimental curves of iodine at 9.8 kb (Teflon container).

FIG. 6.—Phase diagram of iodine.

but the pressure differences are 2, 5, 9, and 13 kb at 300, 400, 500, and 600°C, respectively (our pressures are lower at a given temperature). There are several differences concerning the technique applied, only a few of which will be mentioned here.

The determination of the so-called "true" pressure is different. Klement *et al.* took as the true pressure the mean between the pressures at which signals were observed on compression and decompression in their work. This pressure calibration method has been popularized by Kennedy and his co-workers. However, it has been shown that the friction on the up- and downstrokes is not symmetrical, and the simple averaging method cannot be applied to the high-pressure furnaces in our work.¹ Therefore, the calibration values were determined and applied as described in the *General Technique*. However, these differences in pressure calibration cannot account for most of the observed discrepancies in the phase diagrams.

The major discrepancy appears to be in the determination of the melting temperature. The true melting temperature at a particular pressure of iodine was determined from the heating curves in the present work. On the other hand, it seems that the melting temperatures were determined at freezing on the compression stroke at a constant temperature in the work of Klement *et al.* In the present work the DTA signals on cooling were so large and wide that it was difficult to determine the exact solidification temperature of iodine. However, by examining our DTA curves it was found, interestingly enough, that the cooling temperatures which corresponded to our DTA peaks fell on a curve drawn through the melting points given by Klement *et al.* The melting temperatures found are 223, 290, 326, and 368°C at 4.8, 7.6, 9.8, and 12.4 kb, respectively.

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